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(54) Title: PARTIAL SYNTHETIC TRANSMISSION FLUIDS WITH IMPROVED LOW TEMPERATURE PROPERTIES

(57) Abstract

This invention relates to a composition and method for producing partial synthetic transmission fluids having a -40 °C Brookfield viscosity no greater than 10,000, preferably no greater than 5,000 centipoise without the need to incorporate viscosity modifying amounts of high molecular weight polymeric viscosity modifiers.

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PARTIAL SYNTHETIC TRANSMISSION FLUIDS WITH IMPROVED LOW TEMPERATURE PROPERTIES

This invention relates to compositions and methods of improving properties of transmission fluids, particularly to obtaining partial synthetic automatic transmission fluids of improved low temperature properties.

Automobile manufacturers continue to seek ways to improve automatic transmission operation, especially at low temperature, through advances in automatic transmission fluid (ATF) technology. Improvements in transmission operation at low temperatures are accomplished by lowering the allowable viscosity of the ATF at -40°C, as measured by a Brookfield viscometer. Historically, the maximum allowable Brookfield viscosity at -40°C of an ATF was 50,000 centipoise (cP). This upper limit existed until approximately 1990, when it was reduced to 20,000 cP. This dramatic reduction in viscosity at low temperatures significantly improved transmission operation, which has been well documented (SAE paper 870356 (1987)). More recently, -40°C viscosity limits have been further reduced to a maximum of 15,000 cP, and in some applications to no more than 5,000 cP.

Meeting these very stringent low temperature requirements has been the focus of much research into basestock quality, synthetic base oils, and flow improvers. We have now found that merely adding synthetic base oils to conventional mineral oils, viscosities in the range of 5,000-10,000 cP cannot be achieved without the incorporation of a "flow improver". A "flow improver", sometimes referred to as a pour point depressant, is a compound that influences the crystallization of wax in the lubricating oil as the temperature is decreased. More specifically, the "flow improver" modifies the crystal structure of the wax such that it cannot form "gel structures" in the lubricant. This phenomenon is well known and is described in, for example, "Crystal-Growth Poisoning of N-Paraffin Wax by Polymeric Additives and its Relevance to Polymer Crystallization Mechanisms", G. A. Holder and J. Winkler, Nature, 207 (4996) 719-21. What has previously not been reported is the dramatic adverse effect of the wax on the -40°C viscosity of partially synthetic ATF's.

This invention overcomes this low temperature problem by providing partially synthetic ATF's with -40°C viscosities approaching the theoretical viscosities of wax-free ATF's, i.e., fully synthetic ATF's.

SUMMARY OF THE INVENTION

This invention relates to a transmission fluid comprising:

(a) a natural lubricating oil having a kinematic viscosity from 2.0 to 8.0 mm^2/s at 100°C;

(b) a synthetic lubricating oil having a kinematic viscosity from 2 to 100 mm^2/s at 100°C;

(c) a seal swelling agent;

(d) 0.001 - 5.0 weight percent of a friction modifier; and

(e) 0.05 to 2.0 weight percent of a non-wax gelling flow improver;

providing the fluid has a kinematic viscosity of at least 3.8 mm^2/s at 100°C and a Brookfield viscosity of no greater than 10,000 centipoise at -40°C.

An advantage of this invention is that the transmission fluid produced does not derive significant kinematic viscosity from high molecular weight polymeric viscosity modifiers.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a combination which uniquely produces a transmission fluid with Brookfield viscosities of less than 10,000 cP, and in some cases less than 5,000 cP. In addition, these fluids do not contain viscosity modifying amounts of high molecular weight polymeric viscosity modifiers. That is, they do not derive any significant amount (i.e., less than 2,

preferably less than 1 mm^2/s (cSt) at 100°C) of their kinematic viscosity at 100°C from polymeric thickeners.

Natural Lubricating Oils

Natural lubricating oils include animal oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. Typically, these oils will have kinematic viscosities of from 2.0 mm^2/s (cSt) to 8.0 mm^2/s (cSt) at 100°C. More preferably the natural lubricating oil will have a kinematic viscosity at 100°C of from about 3.0 and 5.0 mm^2/s (cSt).

The preferred natural lubricating oil is mineral oil. This includes oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlordiethyl ether, etc. They may be hydrotreated or hydrofined, dewaxed by chilling or catalytic processes, or hydrocracked. The base oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes.

Typically, the transmission fluid will contain from 1 to 80, preferably from 10 to 75, more preferably from 20 to 50 weight percent natural lubricating oil.

Synthetic Lubricating Oils

The synthetic lubricating oils used in this invention are one of any number of commonly used synthetic hydrocarbon base oils which include, but are not limited to, polyalphaolefins, alkylated aromatics, and mixtures thereof. Examples of these oils are polymerized and interpolymerized olefins (e.g., polybutenes, polypropylenes, polypropylene-isobutylene copolymers, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); alkylated diphenyl ethers and derivatives, analogs and homologs thereof.

Particularly preferred synthetic oils are the polyalphaolefins, especially those polyalphaolefins produced by oligomerizing 1-octene and 1-decene.

The synthetic oils used in this invention will typically have kinematic viscosities of between 2 and 100 mm^2/s (cSt) at 100°C, with the most preferred oils having viscosities in the range of 2 to 6 mm^2/s (cSt) at 100°C.

Typically, the transmission fluid will contain from 2 to 80 weight percent, preferably from 10 to 75, and most preferably from 30 to 60 weight percent of the synthetic lubricating oil.

Seal Swell Agents

The seal swell agents useful with this invention are esters, alcohols, substituted sulfolanes, or mineral oils that cause swelling of elastomeric materials. The ester based seal swellers of this invention would include esters of monobasic and dibasic acids with monoalcohols, or esters of polyols with monobasic acids. Examples of ester type seal swelling agents are: diisooctyl adipate, dioctyl sebacate, di-isooctyl azelate, dioctyl phthalate, di-hexyl phthalate. Alcohol type seal swellers are linear alkyl alcohols of low volatility. Examples of suitable alcohols are decyl alcohol, tridecyl alcohol and tetradecyl alcohol. Examples of substituted sulfolanes are described in U.S. Patent 4,029,588. Mineral oils useful as seal swellers are typically low viscosity mineral oils with high naphthenic or aromatic content. Examples of suitable mineral oils are Exxon Necton-37 (FN 1380) and Exxon Mineral Seal Oil (FN 3200). Typical fluids produced by this invention will contain from about 1 to about 30 weight percent seal sweller. Preferred ranges of seal sweller are from about 2 to about 20 weight percent and most preferred are from about 5 to about 15 weight percent.

Non-Wax Gelling Flow Improvers

The flow improvers of the current invention are oil soluble polymers that modify the crystallization of any wax contained in the lubricating oil so that "gelling" of the lubricating oil is prevented, and viscosity increase at low temperature is minimized. Thus, for the purposes of this discussion, the expression "non-wax gelling flow improver" refers to a polymer that lowers the -40°C Brookfield viscosity of a wax-containing lubricant. To determine

whether a polymer is a non-wax gelling flow improver, 1.0 mass percent of the polymer is added to a wax-containing lubricant blend. The -40°C Brookfield viscosities of the lubricant with and without the flow improver are then measured. For a polymer to be a non-wax gelling flow improver, the -40°C viscosity of the blend containing the flow improver must be lower than the corresponding blend without the flow improver.

The non-wax gelling flow improvers act by modifying the size, number, and growth of wax crystals in lubricating oils in such a way as to impart improved low temperature handling, pumpability, and or transmission operability. There are two common types of polymers used as flow improvers — one derives its activity from the backbone, the other from the sidechain.

The active backbone variety, such as ethylene-vinyl acetate (EVA) co-polymers, have various lengths of methylene segments randomly distributed in the backbone of the polymer. These ethylenic segments, which associate or co-crystallize with the wax crystals, inhibit further crystal growth due to branches and non-crystallizable segments in the polymer.

The active sidechain type polymers, which are the preferred flow improvers for this invention, have methylene segments in the side chains, preferably normal alkyl groups. These polymers work similarly to the active backbone type except the side chains have been found to be more effective in treating isoparaffins as well as n-paraffins found in lubricating oils. Representative of this type of polymer are C_8 to C_{18} dialkylfumarate vinyl acetate copolymers, polyacrylates, polymethacrylates, and esterified styrene-maleic anhydride copolymers.

While the polyacrylates, polymethacrylates, and styrene-maleic anhydrides may function as viscosity modifiers (i.e., polymeric compositions used to increase the viscosity index of lubricating compositions), it is appreciated by those skilled in the art that these compositions also function as flow improvers depending on their molecular weight and treat rate. Thus, for the purposes of this invention, non-wax gelling flow improvers include polyacrylates, polymethacrylates, and styrene-maleic anhydrides having average molecular weights no greater than 500,000 atomic mass units as determined, for example, by gel permeation chromatography. The term

"atomic mass unit" is a measure of atomic mass defined as 1/12 the mass of a carbon atom of mass 12.

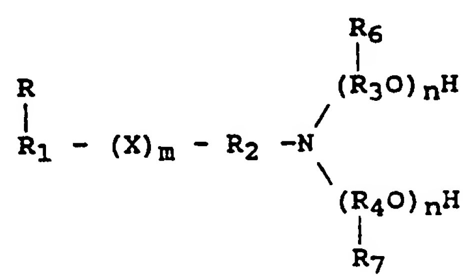
Typically, products of this invention will contain from 0.05 to about 2.0 weight percent flow improver. Preferred concentrations of flow improvers are from about 0.1 to about 2.0 weight percent and most preferred are from about 0.2 to about 2.0 weight percent.

Friction Modifiers

A wide variety of friction modifiers may be employed in the present invention including the following:

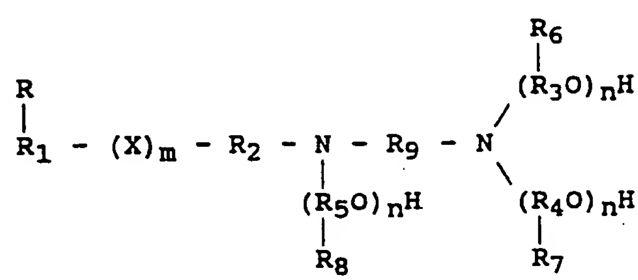
(i) Alkoxylated Amines

Alkoxylated amines are a particularly suitable type of friction modifier for use in this invention. These types of friction modifiers may be selected from the group consisting of (I), (II), and mixtures thereof, where (I) and (II) are:



(I)

and



(II)

where:

R is H or CH_3;

R_1 is a C_8-C_{28} saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbyl radical, preferably C_{10}-C_{20}, most preferably C_{14}-C_{18};
R_2 is a straight or branched chain C_1-C_6 alkylene radical, preferably C_2-C_3;
R_3, R_4, and R_5 are independently the same or different, straight or branched chain C_2-C_5 alkylene radical, preferably C_2-C_4;
R_6, R_7, and R_8 are independently H or CH_3;
R_9 is a straight or branched chain C_1-C_5 alkylene radical, preferably C_2-C_3;
X is oxygen or sulfur, preferably oxygen; m is 0 or 1, preferably 1; and
n is an integer, independently 1-4, preferably 1.

In a particularly preferred embodiment, this type of friction modifier is characterized by formula (I) where X represents oxygen, R and R_1 contain a combined total of 18 carbon atoms, R_2 represents a C_3 alkylene radical, R_3 and R_4 represent C_2 alkylene radicals, R_6 and R_7 are hydrogens, m is 1, and each n is 1. Preferred amine compounds contain a combined total of from about 18 to about 30 carbon atoms.

Preparation of the amine compounds, when X is oxygen and m is 1, is, for example, by a multi-step process where an alkanol is first reacted, in the presence of a catalyst, with an unsaturated nitrile such as acrylonitrile to form an ether nitrile intermediate. The intermediate is then hydrogenated, preferably in the presence of a conventional hydrogenation catalyst, such as platinum black or Raney nickel, to form an ether amine. The ether amine is then reacted with an alkylene oxide, such as ethylene oxide, in the presence of an alkaline catalyst by a conventional method at a temperature in the range of about 90-150°C.

Another method of preparing the amine compounds, when X is oxygen and m is 1, is to react a fatty acid with ammonia or an alkanol amine, such as ethanolamine, to form an intermediate which can be further oxyalkylated by reaction with an alkylene oxide, such as ethylene oxide or propylene oxide. A process of this type is discussed in, for example, U.S. Patent No. 4,201,684.

When X is sulfur and m is 1, the amine friction modifying compounds can be formed, for example, by effecting a conventional free radical reaction between a long chain alpha-olefin with a hydroxyalkyl mercaptan, such as beta-hydroxyethyl mercaptan, to produce a long chain alkyl hydroxyalkyl sulfide. The long chain alkyl hydroxyalkyl sulfide is then mixed with thionyl chloride at a low temperature and then heated to about 40°C to form a long chain alkyl chloroalkyl sulfide. The long chain alkyl chloroalkyl sulfide is then caused to react with a dialkanolamine, such as diethanolamine, and, if desired, with an alkylene oxide, such as ethylene oxide, in the presence of an alkaline catalyst and at a temperature near 100°C to form the desired amine compounds. Processes of this type are known in the art and are discussed in, for example, U.S. Patent No. 3,705,139.

In cases when X is oxygen and m is 1, the present amine friction modifiers are well known in the art and are described in, for example, U.S. Patent Nos. 3,186,946, 4,170,560, 4,231,883, 4,409,000 and 3,711,406.

Examples of suitable amine compounds include, but are not limited to, the following:

N,N-bis(2-hydroxyethyl)-n-dodecylamine;
N,N-bis(2-hydroxyethyl)-1-methyl-tridecenylamine;
N,N-bis(2-hydroxyethyl)-hexadecylamine;
N,N-bis(2-hydroxyethyl)-octadecylamine;
N,N-bis(2-hydroxyethyl)-octadecenylamine;
N,N-bis(2-hydroxyethyl)-oleylamine;
N,N-bis(2-hydroxyethyl)-stearylamine;
N,N-bis(2-hydroxyethyl)-undecylamine;
N-(2-hydroxyethyl)-N-(hydroxyethoxyethyl)-n-dodecylamine;
N,N-bis(2-hydroxyethyl)-1-methyl-undecylamine;
N,N-bis(2-hydroxyethoxyethoxyethyl)-1-ethyl-octadecylamine;
N,N-bis(2-hydroxyethyl)-cocoamine;
N,N-bis(2-hydroxyethyl)-tallowamine;
N,N-bis(2-hydroxyethyl)-n-dodecyloxyethylamine;
N,N-bis(2-hydroxyethyl)-lauryloxyethylamine;
N,N-bis(2-hydroxyethyl)-stearyloxyethylamine;
N,N-bis(2-hydroxyethyl)-dodecylthioethylamine;
N,N-bis(2-hydroxyethyl)-dodecylthiopropylamine;

N,N-bis(2-hydroxyethyl)-hexadecyloxypropylamine;

N,N-bis(2-hydroxyethyl)-hexadecylthiopropylamine;

N-2-hydroxyethyl,N-[N',N'-bis(2-hydroxyethyl) ethylamine] -octadecylamine; and

N-2-hydroxyethyl,N-[N',N'-bis(2-hydroxyethyl) ethylamine] -stearylamine.

The most preferred additive is N,N-bis(2-hydroxyethyl)-hexadecyloxypropylamine. This additive is available from Tomah Company under the designation Tomah E-22-S-2.

The amine's hydrocarbyl chain length, the saturation of the hydrocarbyl chain, and the length and position of the polyoxyalkylene chains can be varied to suit specific requirements. For example, increasing the number of carbon atoms in the hydrocarbyl radical tends to increase the amine's melting temperature and oil solubility, however, if the hydrocarbyl radical is too long, the amine will crystallize from solution. Decreasing the degree of saturation in the hydrocarbyl radical, at the same carbon content of the hydrocarbyl chain, tends to reduce the melting point of the amine. Increasing the amount of alkylene oxide, to lengthen the polyoxyalkylene chains, tends to increase the amine's water solubility and decrease its oil solubility.

The amine compounds may be used as such. However, they may also be used in the form of an adduct or reaction product with a boron compound, such as a boric oxide, a boron halide, a metaborate, boric acid, or a mono-, di-, and trialkyl borate. Such adducts or derivatives may be illustrated, for example, by the following structural formula:

$$
\begin{array}{ccccccc}
R & & & & (R_3O)_n & & \\
| & & & / & & \backslash & \\
R_1 - (X)_m - R_2{-}N & & & & & & B{-}O{-}R_{10} \\
 & & & \backslash & & / & \\
 & & & & (R_4O)_n & &
\end{array}
$$

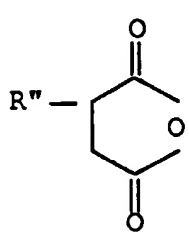
where R, R_1, R_2, R_3, R_4, X, m, and n are the same as previously defined and where R_{10} is either hydrogen or an alkyl radical.

(ii) Carboxylic Acids/Anhydrides with Polyamines

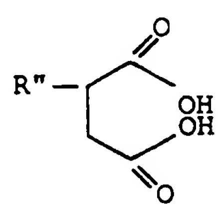
A second type of friction modifier useful with this invention is the reaction product of a polyamine and a carboxylic acid or anhydride. Briefly, the polyamine reactant contains from 2 to 60 total carbon atoms and from 3 to 15 nitrogen atoms with at least one of the nitrogen atoms present in the form of a primary amine group and at least two of the remaining nitrogen atoms present in the form of primary or secondary amine groups. Non-limiting examples of suitable amine compounds include: polyethylene amines such as diethylene triamine (DETA); triethylene tetramine (TETA); tetraethylene pentamine (TEPA); polypropylene amines such as di-(1,2-propylene)triamine, di(1,3-propylene) triamine, and mixtures thereof. Additional suitable amines include polyoxyalkylene polyamines such as polyoxypropylene triamines and polyoxyethylene triamines. Preferred amines include DETA, TETA, TEPA, and mixtures thereof (PAM). The most preferred amines are TETA, TEPA, and PAM.

The carboxylic acid or anhydride reactant of the above reaction product is characterized by formula (III), (IV), (V), (VI), and mixtures thereof:

$$R'' - \overset{\displaystyle O}{\overset{\|}{C}} - OH \qquad (III); \qquad R'' - \overset{\displaystyle O}{\overset{\|}{C}} - O - \overset{\displaystyle O}{\overset{\|}{C}} - R'' \qquad (IV);$$



(V); and



(VI)

where R" is a straight or branched chain, saturated or unsaturated, aliphatic hydrocarbyl radical containing from 9 to 29 carbon atoms, preferably from 11 to 23. When R" is a branched chain group, no more than 25% of the carbon atoms are in side chain or pendent groups. R" is preferably straight chained.

The R" hydrocarbyl group includes predominantly hydrocarbyl groups as well as purely hydrocarbyl groups. The description of these groups as predominantly hydrocarbyl means that they contain no non-hydrocarbyl substituents or non-carbon atoms that significantly affect the hydrocarbyl characteristics or properties of such groups relevant to their uses as described here. For example, a purely hydrocarbyl C_{20} alkyl group and a C_{20} alkyl group substituted with a methoxy substituent are substantially similar in their properties and would be considered hydrocarbyl within the context of this disclosure.

Non-limiting examples of substituents that do not significantly alter the hydrocarbyl characteristics or properties of the general nature of the hydrocarbyl groups of the carboxylic acid or anhydride are:

Ether groups (especially hydrocarbyloxy such as phenoxy, benzyloxy, methoxy, n-isotoxy, etc., particularly alkoxy groups of up to ten carbon atoms);

Oxo groups (e.g., -O- linkages in the main carbon chain);

Ester groups (e.g., $-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O-hydrocarbyl}$);

Sulfonyl groups (e.g., $-\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{hydrocarbyl}$); and

Sulfinyl groups (e.g., $-\underset{\underset{\text{O}}{\|}}{\text{S}}-\text{hydrocarbyl}$).

These types of friction modifiers can be formed by reacting, at a temperature from about 120 to 250°C, at least one polyamine and one carboxylic acid or anhydride in proportions of about 2 to 10 molar equivalents of carboxylic acid or anhydride per mole of amine reactant.

(iii) Other Friction Modifiers

Optionally, other friction modifiers may be used either alone or in combination with the foregoing described friction modifiers to achieve the desired fluid performance. Among these are esters of carboxylic acids and anhydrides with alkanols. Other conventional friction modifiers generally consist of a polar terminal group (carboxyl, hydroxyl, amino, etc.) covalently bonded to an oleophilic hydrocarbon chain.

Particularly preferred esters of carboxylic acids and anhydrides with alkanols are described in, for example, U.S. Patent 4,702,850. This reference teaches the usefulness of these esters as friction modifiers, particularly the esters of succinic acids or anhydrides with thio-bis-alkanols, most particularly with esters of 2-octadecenyl succinic anhydride and thiodiglycol.

Examples of other conventional friction modifiers (i.e., polar terminal group + oleophilic hydrocarbon chain) are described by, for example, M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26.

Typically the friction modifiers will be present in finished transmission fluid composition in an amount between 0.01 to 5, preferably 0.1 to 3 weight percent.

Other Additives

Other additives known in the art may be added to the transmission fluid. These additives include dispersants, antiwear agents, antioxidants, corrosion inhibitors, detergents, extreme pressure additives, and the like. They are typically disclosed in, for example, "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith, 1967, pp. 1-11 and U.S. Patent 4,105,571.

Representative amounts of these additives are summarized as follows:

Additive	(Broad) Wt.%	(Preferred) Wt.%
Corrosion Inhibitor	0.01 - 3	0.02 - 1
Antioxidants	0.01 - 5	0.2 - 3
Dispersants	0.10 - 10	2 - 5
Antifoaming Agents	0.001- 1	0.001 - 0.5
Detergents	0.01 - 6	0.01 - 3
Antiwear Agents	0.001- 5	0.2 - 3

Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Mixtures of such dispersants can also be used.

The preferred dispersants are the alkenyl succinimides. These include acyclic hydrocarbyl substituted succinimides formed with various amines or amine derivatives such as are widely disclosed in the patent literature. Use of alkenyl succinimides which have been treated with an inorganic acid of phosphorus (or an anhydride thereof) and a boronating agent are also suitable for use in the compositions of this invention as they are much more compatible with elastomeric seals made from such substances as fluoro-elastomers and silicon-containing elastomers. Polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and an alkylene polyamine such as triethylene tetramine or tetraethylene pentamine wherein the polyisobutenyl substituent is derived from polyisobutene having a number average molecular weight in the range of 500 to 5000 (preferably 800 to 2500) are particularly suitable. Dispersants may be post-treated with many reagents known to those skilled in the art. (see, e.g., U.S. Pat. Nos. 3,254,025, 3,502,677, and 4,857,214).

Suitable antioxidants are amine-type and phenolic antioxidants. Examples of the amine-type antioxidants include phenyl alpha naphthylamine, phenyl beta naphthylamine, diphenylamine, bis- alkylated diphenyl amines (e.g., p,p'-bis(alkylphenyl)amines wherein the alkyl groups contain from 8 to 12 carbon atoms each). Phenolic antioxidants include sterically hindered phenols (e.g., 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, etc.) and bis-phenols (e.g., 4,4'- methylenebis(2,6-di-tert-butylphenol), etc.) and the like.

The additive concentrates of this invention will contain the viscosity modifier, friction modifier, and other desired additives in a natural and/or synthetic lubricating oil, in relative proportions such that by adding the concentrate to a larger amount of a suitable natural and/or synthetic oil the resulting fluid will contain each of the ingredients in the desired concentration. Thus, the concentrate may contain a synthetic oil as the lubricating oil if the desired final composition contains a lesser amount of synthetic oil relative to the mineral oil. The concentrate typically will contain between 25 to 100, preferably from 65 to 95, most preferably from 75 to 90 weight percent of the viscosity modifier, friction modifier, other desired additives, and synthetic and/or natural oil.

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. Although the following examples are directed to automatic transmission fluids (ATF), this invention is also equally applicable to powershift transmissions, manual transmissions, hydrostatic transmissions, continuously variable transmissions, and the like. All parts and percentages in the examples as well as in the remainder of the specification and claims are by weight unless otherwise specified.

EXAMPLE 1

Table 1 shows nineteen (19) automatic transmission fluids (BLENDS 1-19) that were produced by blending 8.0 mass percent of an additive package devoid of any flow improvers, into suitable ATF base oils. The additive package contained conventional amounts of a succinimide dispersant, antioxidants, antiwear agents, friction modifiers, a corrosion inhibitor, an antifoamant, and a diluent oil.

Each ATF contained Exxon solvent 100 neutral oil (≈4.0 mm^2/s (cSt) at 100°C) (FN 1365) and PAO-4 (≈4.0 mm^2/s (cSt) at 100°C) (1-decene oligomer). The ratio of 100 neutral oil to PAO-4 was chosen such that a properly treated blend could achieve a -40°C viscosity of less than 10,000 cP, and a kinematic viscosity at 100°C of at least 3.8 mm^2/s (cSt). Additionally, BLENDS 1-19 contained diisooctyl adipate as a seal swelling

agent. The compositions of the blends and their measure kinematic viscosities at 100°C and Brookfield viscosities at -40°C are shown in Table 1.

The flow improvers used are identified in Table 1 by their trade names. The PARAFLOW® products are fumarate-vinyl acetate copolymers with varying sidechain lengths. The ACRYLOID®, TLA (Texaco) and VISCOPLEX® products are polymethacrylates of varying molecular weights and sidechain lengths.

BLEND 1 in Table 1 is a 'blank' in that it contains no flow improver. As shown, this blend has a very high -40°C Brookfield viscosity of 87,000 cP which is totally unexpected for an ATF containing over 40% of a synthetic lubricating oil, PAO-4. In addition, BLENDS 8 and 9 show the results obtained when an ineffective flow improver is used. While not wishing to be bound to any particular theory, it is believed that the PARAFLOW 394 flow improver used in BLENDS 8 and 9 polymerizes with the wax present in the natural lubricating oil to form a crosslinked wax gel which causes viscosities at -40°C higher than those of the 'blank'. However, all of the other "flow improvers" in Table 1 provide a significant reduction in -40°C Brookfield viscosity relative to the 'blank'. As shown, some flow improvers are more effective than others; compare BLENDS 4 and 10, both at 1.00 percent treat rate, and BLENDS 3 and 5 both at 0.25 percent treat with essentially equal kinematic viscosities at 100°C. Thus, Table 1 demonstrates the dramatic effect that certain flow improvers, specifically the non-wax gelling flow improvers of this invention, can have on the -40°C Brookfield viscosity of partial synthetic ATF's.

<u>EXAMPLE 2</u>

Fluid viscosity at -40°C is not only a function of flow improver type but also flow improver concentration. Table 2 shows a series of blends using three effective flow improvers for this system. Table 2 shows that for each flow improver there is an optimum treat rate to obtain the lowest -40°C Brookfield viscosity (see BLENDS 23, 27, and 31). While not wishing to be bound to any particular theory, it is believed that this result occurs because there is not enough flow improver at very low concentration to disrupt crystallization of all the wax and consequently the Brookfield viscosities are elevated compared to the minimum Brookfield viscosity obtainable in these

systems (see BLENDS 24, 28, 29 and 34). It is also believed that at concentrations that are too high, the flow improver merely adds viscosity at -40°C since the flow improver is itself a polymer (see BLENDS 21, 26 and 30). Therefore, for each ATF system, the type and concentration of the most effective flow improver must be determined.

EXAMPLE 3

Table 3 shows a number of ATF blends made using the Exxon solvent 100 neutral oil that produce fluids that completely meet very stringent targets, i.e., kinematic viscosity at 100°C of no less than 3.8 mm^2/s (cSt) and Brookfield viscosities at -40°C less than 5,000 cP. BLENDS 37, 39, 42, 43, 44, 45, and 46 fully meet these stringent requirements, this is only possible due to the incorporation of non-wax gelling flow improvers.

EXAMPLE 4

The compositions of this invention work in a variety of lubricating oils. Table 4 shows blends meeting the stringent requirements described in Example 3, but with various natural lubricating oils: Exxon 100 neutral (≈4.0 mm^2/s (cSt) at 100°C); Exxon 75 neutral (≈3.0 mm^2/s (cSt) at 100°C); Chevron RLOP 100 neutral — a severely hydrotreated and catalytically de-waxed basestock having a kinematic viscosity of ≈4.1 mm^2/s (cSt) at 100°C; and Imperial MXT-5 — a basestock produced by isomerizing slack wax having a kinematic viscosity of ≈3.8 mm^2/s (cSt) at 100°C. In each case, the composition was evaluated without a flow improver, BLENDS 47, 52, 56, 60 and all show the unexpectedly high -40°C Brookfield viscosities exhibited by mixtures of mineral oils and synthetics without flow improvers. Table 4 shows that any of these natural lubricating oils, when treated with synthetic components and flow improvers, can be made to meet the most restrictive requirements of high and low temperature viscometrics. This is exemplified by BLENDS 49, 51, 53, 55, 57, 59, 61, and 63, all of which have kinematic viscosities at 100°C of at least 3.8 mm^2/s (cSt) and Brookfield viscosities at -40°C under 5,000 cP.

The results in Tables 1 - 4 are unexpected. One skilled in the art would expect that treating a natural lubricating oil based ATF having a -40°C Brookfield viscosity of 20,000 cP with a synthetic lubricating oil having a

-40°C Brookfield viscosity of 2,000 cP to simply produce a fluid with a viscosity in between. However, we have found that the effect of the containing wax in the natural lubricating oil overcomes the beneficial effects of the synthetic lubricating oil and, the wax must be treated with a non-gelling flow improver to obtain all of the expected benefits of a blend containing synthetic lubricating oils (partial synthetic). It is evident even in blends containing only about 25% mineral lubricating oil (BLEND 47), that the untreated wax has a very large negative impact on Brookfield viscosity at -40°C.

The principles, preferred embodiments, and modes of operation of this invention have been described in the foregoing specification. However, the invention which is intended to be protected herein is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

Table 1

EFFECT OF FLOW IMPROVER TYPE

BLENDS:	1	2	3	4	5	6	7	8	9	10
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
EXXON Solvent 100 neutral	40.50	40.00	40.37	40.00	40.37	40.00	40.37	40.00	40.37	40.00
PAO-4	41.50	41.00	41.38	41.00	41.38	41.00	41.38	41.00	41.38	41.00
PARAFLOW 385 *	-	1.00	0.25	-	-	-	-	-	-	-
PARAFLOW 387	-	-	-	1.00	0.25	-	-	-	-	-
PARAFLOW 392	-	-	-	-	-	1.00	0.25	-	-	-
PARAFLOW 394	-	-	-	-	-	-	-	1.00	0.25	-
ACRYLOID 3005 **	-	-	-	-	-	-	-	-	-	1.00
ACRYLOID 3014	-	-	-	-	-	-	-	-	-	-
TLA 5012 ***	-	-	-	-	-	-	-	-	-	-
VISCOPLEX 5011H ****	-	-	-	-	-	-	-	-	-	-
VISCOPLEX 5060	-	-	-	-	-	-	-	-	-	-
VISCOSITY										
Kinematic @ 100 C, cSt	4.29	4.45	4.34	4.43	4.33	4.51	4.35	4.61	4.37	4.49
Brookfield @ -40 C, cP	87,000	7,680	5,120	11,180	6,940	8,060	5,380	320,000	120,000	6,060

* PARAFLOW is a registered trademark of EXXON Chemical Co.

** ACRYLOID is a registered trademark of Rohm & Haas, Corp.

Table 1 (Continued)

EFFECT OF FLOW IMPROVER TYPE

BLENDS:	11	12	13	14	15	16	17	18	19
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
EXXON Solvent 100 neutral	40.37	40.00	40.37	40.00	40.37	40.00	40.37	40.00	40.37
PAO-4	41.38	41.00	41.38	41.00	41.38	41.00	41.38	41.00	41.38
PARAFLOW 385 *	-	-	-	-	-	-	-	-	-
PARAFLOW 387	-	-	-	-	-	-	-	-	-
PARAFLOW 392	-	-	-	-	-	-	-	-	-
PARAFLOW 394	-	-	-	-	-	-	-	-	-
ACRYLOID 3005 **	0.25	-	-	-	-	-	-	-	-
ACRYLOID 3014	-	1.00	0.25	-	-	-	-	-	-
TLA 5012 ***	-	-	-	1.00	0.25	-	-	-	-
VISCOPLEX 5011H ****	-	-	-	-	-	1.00	0.25	-	-
VISCOPLEX 5060	-	-	-	-	-	-	-	1.00	0.25
VISCOSITY									
Kinematic @ 100 C, cSt	4.34	4.47	4.34	4.97	4.46	5.02	4.46	4.72	4.43
Brookfield @ -40 C, cP	5,280	6,300	5,460	5,300	5,460	5,200	5,360	5,260	5,500

*** TLA is a designation of Texaco Chemical Co.

**** VISCOPLEX is a registered trademark of Rohm Darmstadt, Ag.

Table 2

EFFECT OF TREAT RATE

BLENDS:	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
EXXON Solvent 100 neutral	40.50	40.00	40.35	40.37	40.40	40.45	40.00	40.35	40.40	40.45	40.00	40.25	40.35	40.40	40.45
PAO-4	41.50	41.00	41.35	40.38	41.40	41.45	41.00	41.35	41.40	41.45	41.00	41.25	41.35	41.40	41.45
PARAFLOW 385 °	-	1.00	0.30	0.25	0.20	0.10	-	-	-	-	-	-	-	-	-
ACRYLOID 3005 °°	-	-	-	-	-	-	1.00	0.30	0.20	0.10	-	-	-	-	-
TLA 5012 °°°	-	-	-	-	-	-	-	-	-	-	1.00	0.50	0.30	0.20	0.10
VISCOSITY															
Kinematic @ 100 C, cSt	4.29	4.51	N/M	4.34	N/M	4.31	4.49	N/M	N/M	4.32	4.97	4.52	4.47	4.42	N/M
Brookfield @ -40 C, cP	87,000	8,060	5,160	5,120	5,300	5,420	6,060	5,120	6,760	7,800	5,300	5,140	5480	5460	9250

° PARAFLOW is a registered trademark of EXXON Chemical Co.

°° ACRYLOID is a registered trademark of Rohm & Haas, Corp.

°°° TLA is a designation of Texaco Chemical Co.

°°°° VISCOPLEX is a registered trademark of Rohm Darmstadt, Ag.

N/M = Not Measured

Table 3

LOW BROOKFIELD BLENDS

BLENDS:	35	36	37	38	39	40	41	42	43	44	45	46
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
EXXON Solvent 100 neutral	24.60	24.30	24.53	24.30	24.53	24.30	24.30	24.53	24.30	24.53	24.30	24.53
PAO-4	57.40	56.70	57.22	56.70	57.22	56.70	56.70	57.22	56.70	57.22	56.70	57.22
PARAFLOW 385 *	-	1.00	0.25	-	-	-	-	-	-	-	-	-
PARAFLOW 392	-	-	-	1.00	0.25	-	-	-	-	-	-	-
PARAFLOW 394	-	-	-	-	-	1.00	-	-	-	-	-	-
ACRYLOID 3005 **	-	-	-	-	-	-	1.00	0.25	-	-	-	-
TLA 5012 ***	-	-	-	-	-	-	-	-	1.00	0.25	-	-
VISCOPLEX 5011H ****	-	-	-	-	-	-	-	-	-	-	1.00	0.25
VISCOSITY												
Kinematic @ 100 C, cSt	4.25	4.44	4.30	4.45	4.30	4.57	4.41	4.29	4.89	4.41	4.90	4.41
Brookfield @ -40 C, cP	46,500	6,800	3,820	6,140	4,360	96,000	5,020	3,760	3,580	3,580	3,500	4,020

* PARAFLOW is a registered trademark of EXXON Chemical Co.

** ACRYLOID is a registered trademark of Rohm & Haas, Corp.

*** TLA is a designation of Texaco Chemical Co.

**** VISCOPLEX is a registered trademark of Rohm Darmstadt, Ag.

Table 4

EFFECT OF BASE OIL TYPE

BLENDS:	47	48	49	50	51	52	53	54	55
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
PAO-4	57.40	56.70	57.22	56.70	56.70	32.80	32.70	32.40	32.40
PARAFLOW 385 *	-	1.00	0.25	-	-	-	0.25	-	-
PARAFLOW 394	-	-	-	1.00	-	-	-	1.00	-
TLA 5012	-	-	-	-	1.00	-	-	-	1.00
EXXON Solvent 100 Neutral	24.60	24.30	24.53	24.30	24.30	-	-	-	-
EXXON Solvent 75 Neutral	-	-	-	-	-	49.20	49.05	48.60	48.60
CHEVRON RLOP 100 Neutral	-	-	-	-	-	-	-	-	-
IMPERIAL MXT-5	-	-	-	-	-	-	-	-	-
VISCOSITY									
Kinematic @ 100 C, cSt	4.25	4.44	4.30	4.57	4.89	3.79	3.83	4.05	4.40
Brookfield @ -40 C, cP	46,500	6,800	3,820	96,000	3,580	62,000	3,980	268,000	3,700

* PARAFLOW is a registered trademark of EXXON Chemical Co.

** ACRYLOID is a registered trademark of Rohm & Haas, Corp.

Table 4 (Continued)

EFFECT OF BASE OIIL TYPE

BLENDS:	56	57	58	59	60	61	62	63
Additive	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Di-isooctyl Adipate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
PAO-4	49.20	49.05	48.60	48.60	41.00	40.88	40.50	40.50
PARAFLOW 385 *	-	0.25	-	-	-	0.25	-	-
PARAFLOW 394	-	-	1.00	-	-	-	1.00	-
TLA 5012	-	-	-	1.00	-	-	-	1.00
EXXON Solvent 100 Neutral	-	-	-	-	-	-	-	-
EXXON Solvent 75 Neutral	-	-	-	-	-	-	-	-
CHEVRON RLOP 100 Neutral	32.80	32.70	32.40	32.40	-	-	-	-
IMPERIAL MXT-5	-	-	-	-	41.00	40.87	40.50	40.50
VISCOSITY								
Kinematic @ 100 C, cSt	4.26	4.29	4.55	4.89	4.22	4.28	4.54	4.88
Brookfield @ -40 C, cP	82,500	4,080	47,100	4,300	SOLID	4,140	SOLID	4,460

*** TLA is a designation of Texaco Chemical Co.

**** VISCOPLEX is a registered trademark of Rohm Darmstadt, Ag.

CLAIMS:

1. An transmission fluid composition comprising

(a) a natural lubricating oil having a kinematic viscosity from 2.0 to 8.0 mm^2/s at 100°C;

(b) a synthetic lubricating oil having a kinematic viscosity from 2 to 100 mm^2/s at 100°C;

(c) a seal swelling agent;

(d) 0.001 to 5.0 weight percent of a friction modifier; and

(e) 0.05 to 2.0 weight percent of a non-wax gelling flow improver;

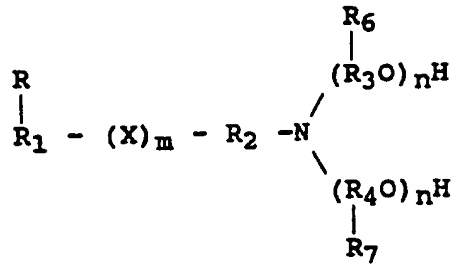
providing the fluid has a kinematic viscosity of at least 3.8 mm^2/s at 100°C and a Brookfield viscosity of no greater than 10,000 centipoise at -40°C.

2. The composition of claim 1 where the synthetic oil is poly-alpha-olefin-, monoester-, diester-, polyolester-based oil, or mixtures thereof.

3. The composition of claim 2 where the oil is a mixture of mineral oil and poly-alpha-olefin.

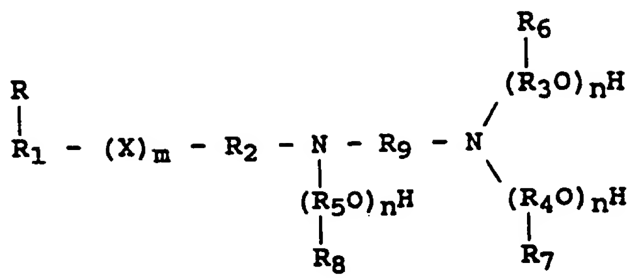
4. The composition of claim 3, where the flow improver is selected from the group consisting of C_8 to C_{18} dialkylfumarate vinyl acetate copolymers, polymethacrylates, polyacrylates, styrene-maleic anhydride copolymers, and their mixtures.

5. The composition of claim 4, wherein the friction modifier is selected from the group consisting of (I); (II); reaction products of polyamines with (III), (IV), (V), (VI); and mixtures thereof, where (I), (II), (III), (IV), (V), (VI) are:

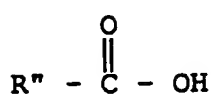


(I)

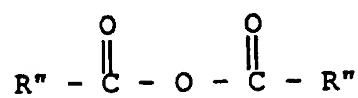
and



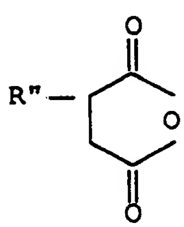
(II)



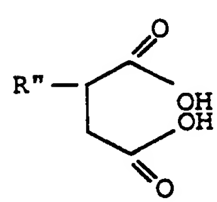
(III);



(IV);



(V); and



(VI)

where:

R is H or CH_3;
R_1 is a C_8-C_{28} saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbyl radical;
R_2 is a straight or branched chain C_1-C_6 alkylene radical;
R_3, R_4, and R_5 are independently the same or different, straight or branched chain C_2-C_5 alkylene radical;
R_6, R_7, and R_8 are independently H or CH_3;
R_9 is a straight or branched chain C_1-C_5 alkylene radical;

X is oxygen or sulfur;
m is 0 or 1;
n is an integer, independently 1-4; and
R" is a straight or branched chain, saturated or unsaturated, aliphatic hydrocarbyl radical containing from 9 to 29 carbon atoms with the proviso that when R" is a branched chain group, no more than 25% of the carbon atoms are in side chain or pendent groups.

6. The composition of claim 5, where the friction modifier is an ethoxylated amine, alkyl amide, or mixtures thereof.

7. The composition of claim 6, where the composition further comprises a borated or non-borated succinimide dispersant, a phenolic or amine antioxidant, such that the sum of the dispersant, antioxidant, and friction modifier is between 2.0 to 11 weight percent of the composition.

8. The composition of claim 1, wherein said composition is an automatic transmission fluid.

9. A method for producing the composition of claim 1 comprising the steps of:

(a) providing a major amount of the natural and synthetic lubricating oil; and

(b) adding to the lubricating oil the flow improver, seal swelling agent, and 0.01 to 5.0 weight percent of the friction modifier.

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/US 96/11681

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M169/04 //(C10M169/04,101:02,105:32,107:10,107:00,129:06,
129:72,133:08,145:10,145:14),C10N40:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 267 098 (ETHYL PETROL. ADDITIVES INC.) 24 November 1993 see page 52; example 6; table III see page 39, line 19 - page 40, line 3	1-9
A	FR,A,2 501 224 (NYCO SA) 10 September 1982 see page 10-11	1-9
A	EP,A,0 454 395 (ETHYL PETROLEUM ADDITIVES) 30 October 1991 see the whole document	1-9
A	EP,A,0 259 808 (IDEMITSU KOSAN CO.LTD) 16 March 1988 see page 8; example 4; table 3	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
16 October 1996	30.10.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rotsaert, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/11681

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2267098	24-11-93	CA-A- 2095972	23-11-93
		DE-A- 4317105	25-11-93
FR-A-2501224	10-09-82	NONE	
EP-A-454395	30-10-91	DE-D- 69119823	04-07-96
		DE-T- 69119823	02-10-96
		US-A- 5387346	07-02-95
EP-A-259808	16-03-88	JP-B- 7030345	05-04-95
		JP-A- 63066295	24-03-88
		CA-A- 1286651	23-07-91
		DE-A- 3778460	27-05-92
		WO-A- 8802020	24-03-88
		US-A- 4960542	02-10-90